Nano Si anodes

Prof. ***Gleb Yushin***

Alexandre Magasinski[a], Bogdan Zdyrko[b], Benjamin Hertzberg[a], Patrick Dixon[a], Frank Grant Jones[a], Jorge Ayala[d], Thomas F. Fuller[c], Igor Luzinov[b] and Gleb Yushin[a]

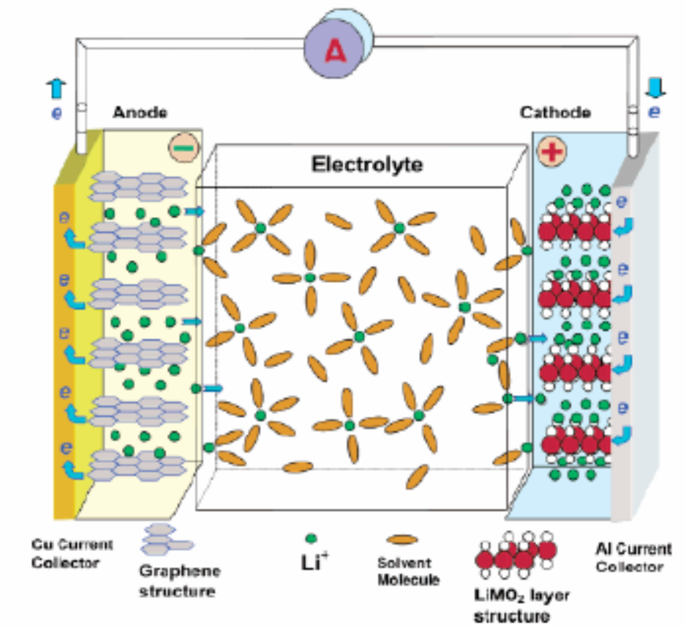
a - School of Materials Science & Engineering, Georgia Institute of Technology,
b - Department of Material Science, Clemson University,
c - School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA
d- Superior Graphite, Chicago, IL

Support:

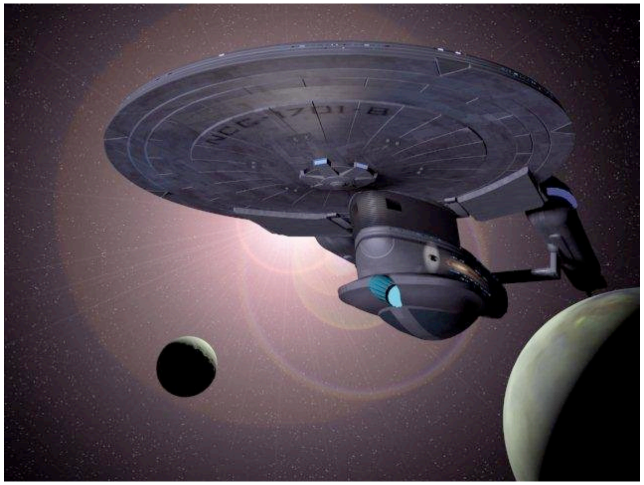
NASA Contract # NNC08CB01C

NASA Contract # NNX09CD29P

Li-ion Batteries



Power for Electronics, Electric cars and HEV



Power for Aerospace

- Higher capacity of electrodes leads to higher **Specific Energy** of Li-ion batteries
- Fast Li transport within electrodes leads to higher **Specific Power** of Li-ion batteries

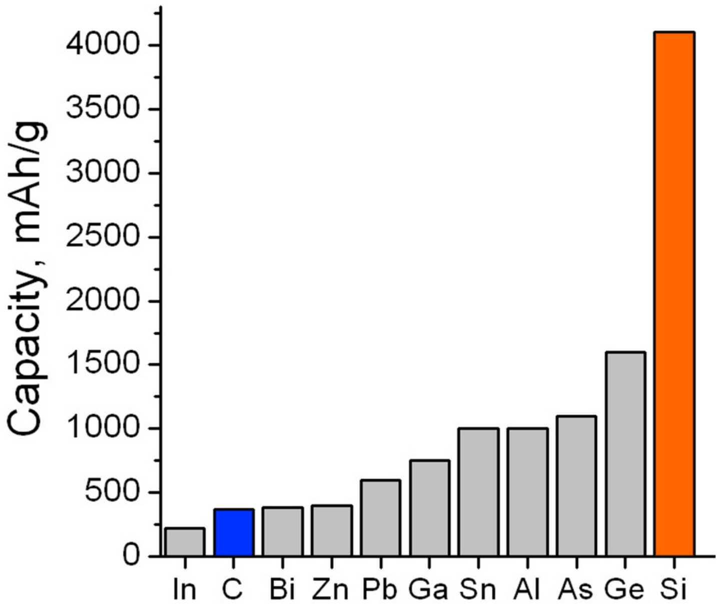
High Capacity Anodes for Li-ion Batteries

- Replacing Graphite by Silicon will increase specific capacity by up to 10 times

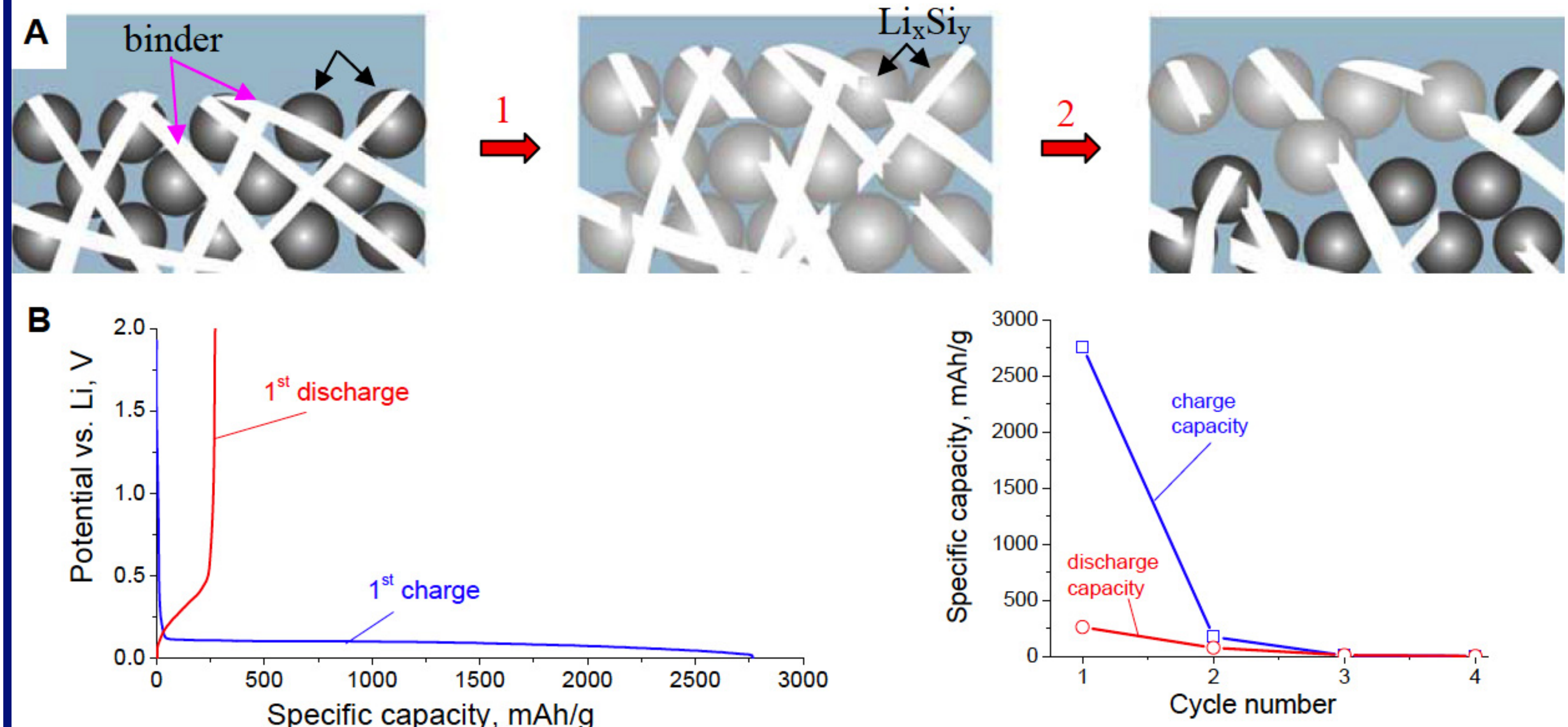
- But… simple replacement of C particles by Si particles does NOT work due to rapid electrode degradation

- Main reason: 4x volume changes in Si particles upon Li insertion and extraction

- Additional issue: low conductivity of Si and low diffusion coefficient of Li in Si



Problems with Si Anodes: Binder Degradation



➢ No binder has been demonstrated to offer acceptable performance when used in Si anodes

Strategies

Novel binders

(1)

Novel **Si-C composite** particles which **do NOT change volume** and thus do NOT require special binders

(2)

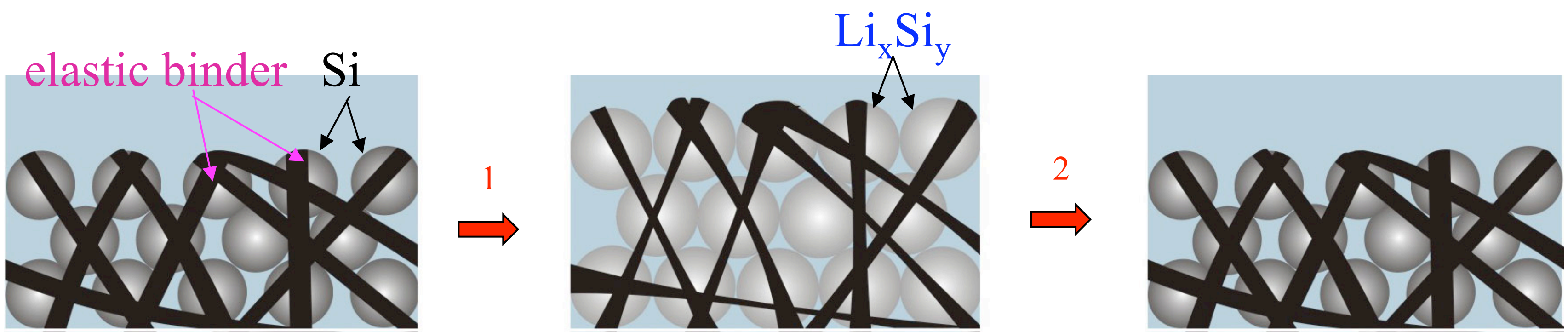
Binders-FREE electrodes

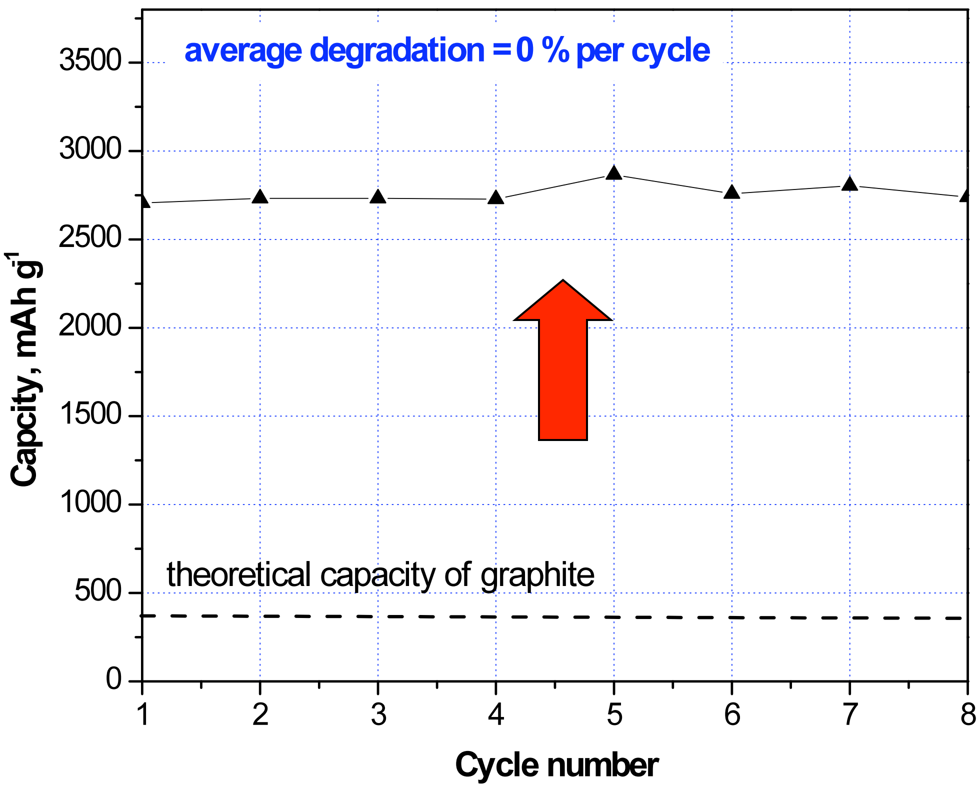
(3)

(1) Novel Binders

NASA Contract # NNC08CB01C

Novel Binders for Si Anodes





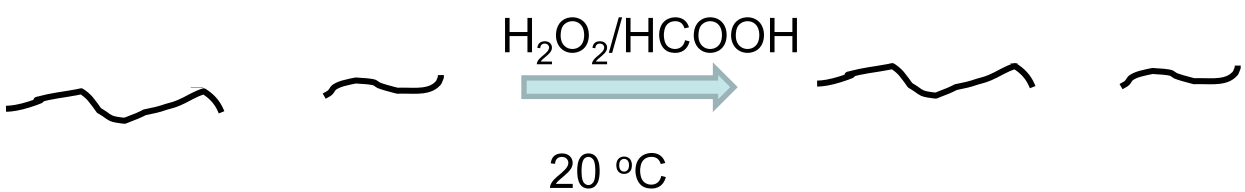
•Performance of the Si anodes based on novel binders can be greatly superior to that o f the traditional graphitic anodes

* - Capacity is based on the weight of the active material (Si)

Novel Binders for Si Anodes

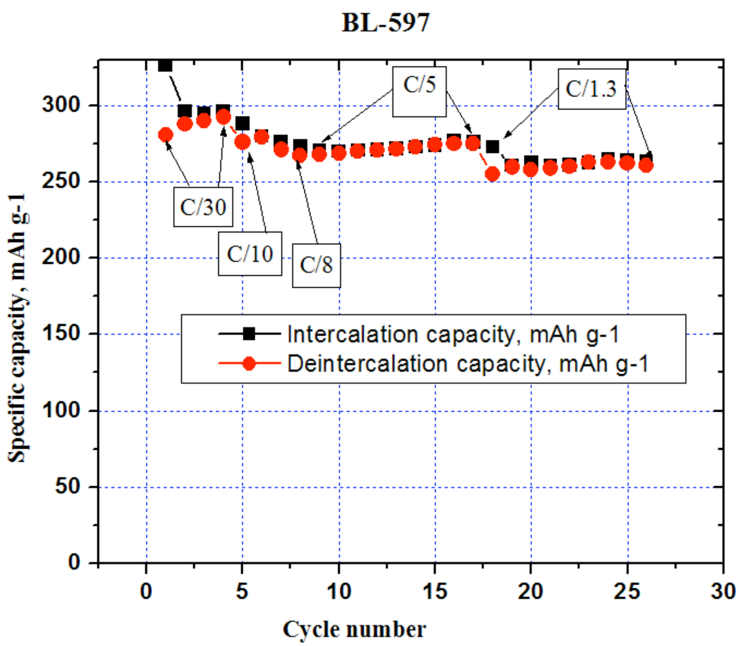
Initial approach: EPB

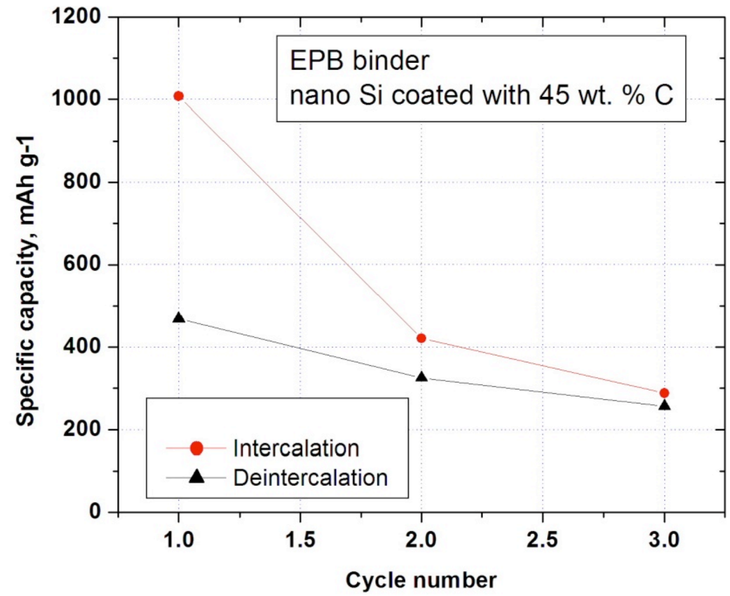
- Epoxidized polybutadiene (EPB) - low cost binder
- Optimize mechanical, adhesion and other properties of the EPB
- Copolymers with various monomers are available
- Crosslinking can be done in dual way: residual double bonds can be reacted radically; created epoxy groups can be crosslinked thermally
- Glass Transition Temperature can be as low as – 100C



- Degree of epoxidation can be tuned via reaction time
- Epoxy groups will enhance adhesion of the binder to Si, carbon and Cu

Novel Binders for Si Anodes: EPB



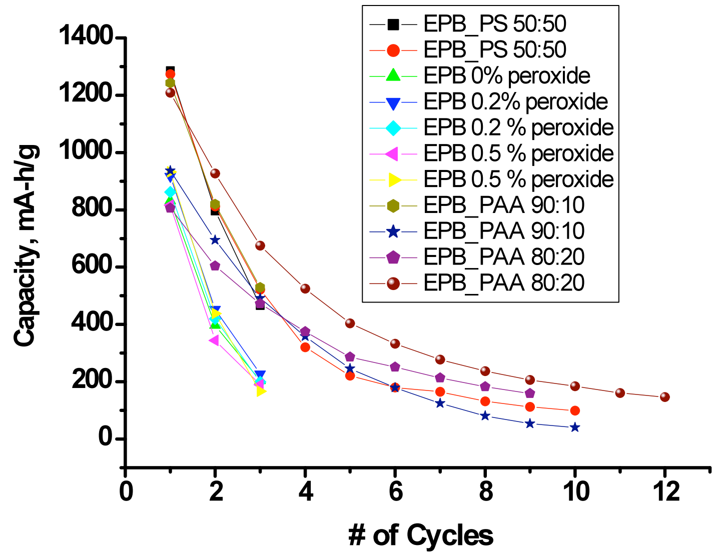


EPB/Graphite electrodes

EPB/nano Si electrodes

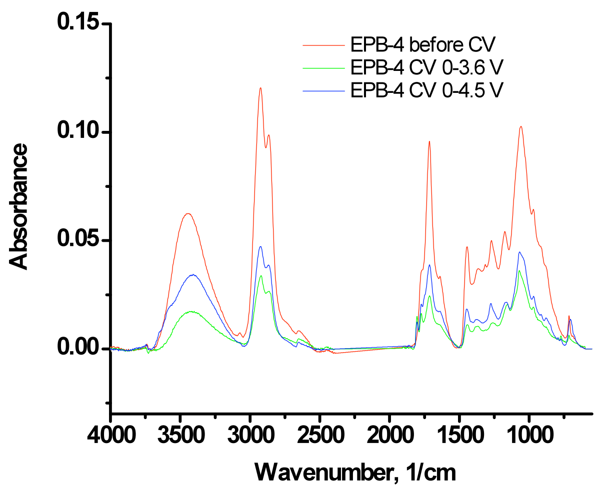
- Good performance with carbon active material
- Rapid degradation with Si
- Huge Irreversible Capacity losses (not stable SEI)

Novel Binders for Si Anodes: EPB

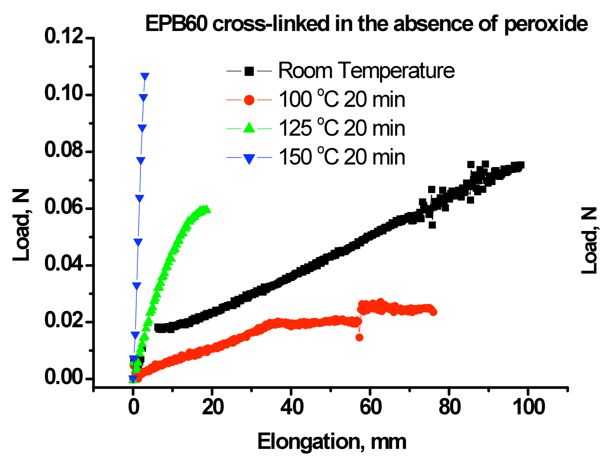


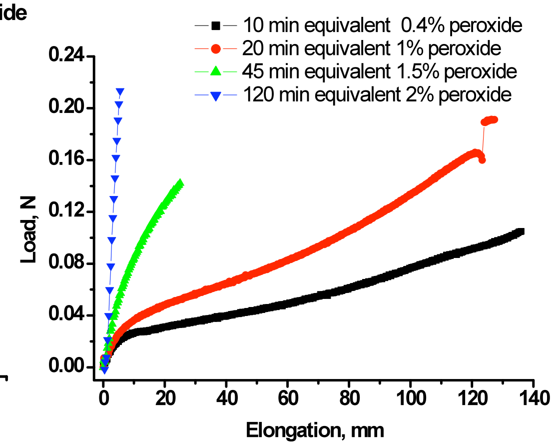
- ➢ EPB is electrochemically stable
- ➢ Variations of mechanical properties do NOT improve anode performance
- ➢ Porosity does NOT affect cycling properties of the anode

Electrochemical stability



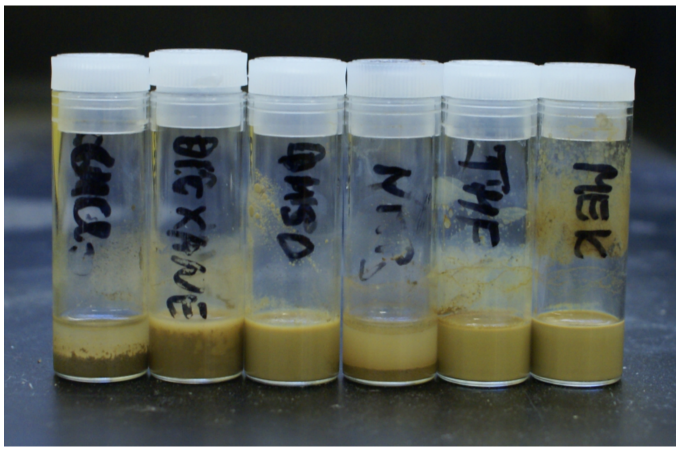
Mechanical properties (porosity) of the EPB binder

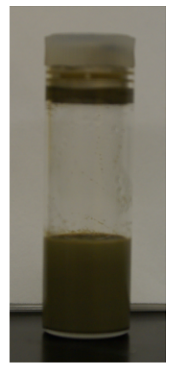




Novel Binders for Si Anodes: EPB

Dispersivity issues?





- With optimized we obtained suspensions <u>stable for days</u>
- Electrodes – very uniform
- But…. Dramatic improvements in dispersvity do NOT improve anode performance

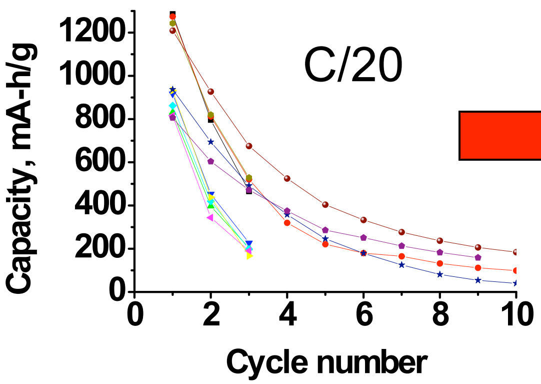
- But... **Why EPB does NOT work?**
- Si-binder interface is the key!!!

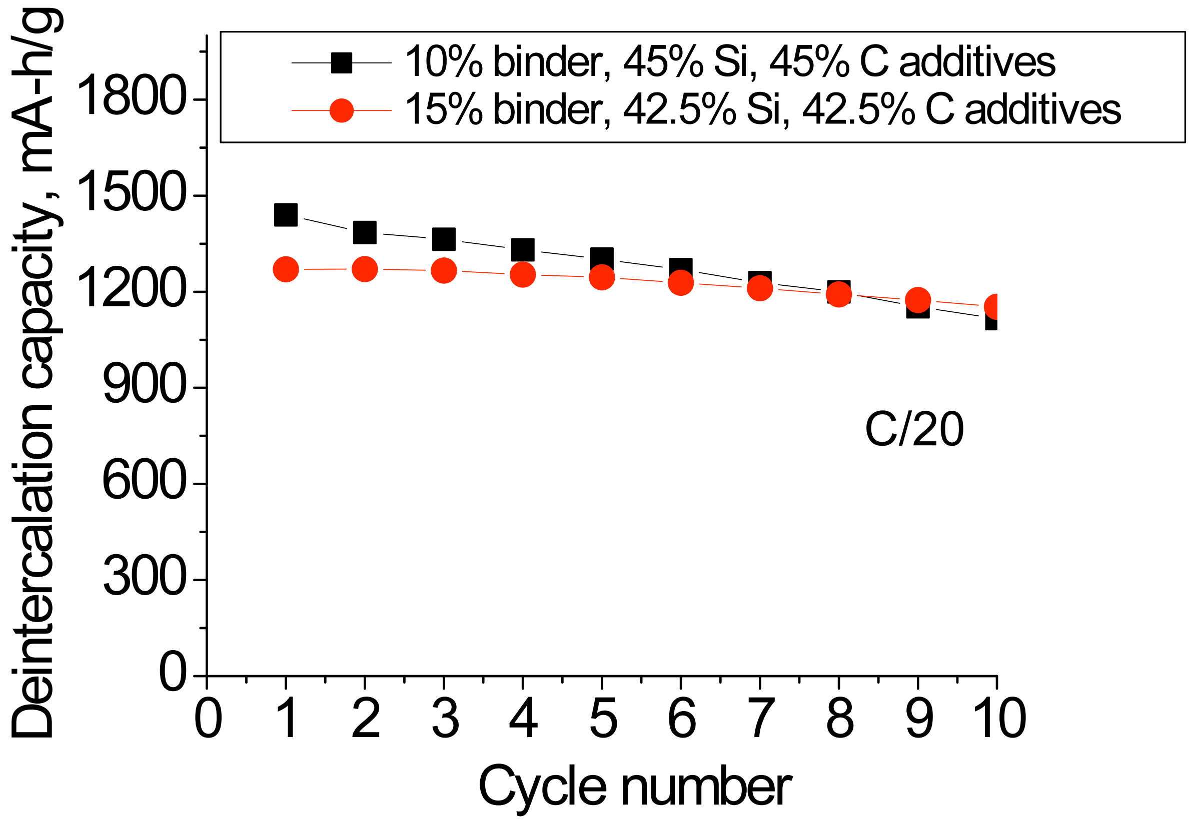
Novel Binders for Si Anodes

- **Solubility in organic** but ecologically friendly **solvents** – Si surface will not get oxidized
- Very **high concentration** of “good/useful” **functional groups** – Si surface can be fully coated/protected with these groups
- **Tunable mechanical properties, and solubility** (via co-polymerization with other functional monomers) – can optimize the performance
- Can **regulate the molecular weight** – can optimize the performance

** - provisional US patent filed*

Novel Binders for Si Anodes





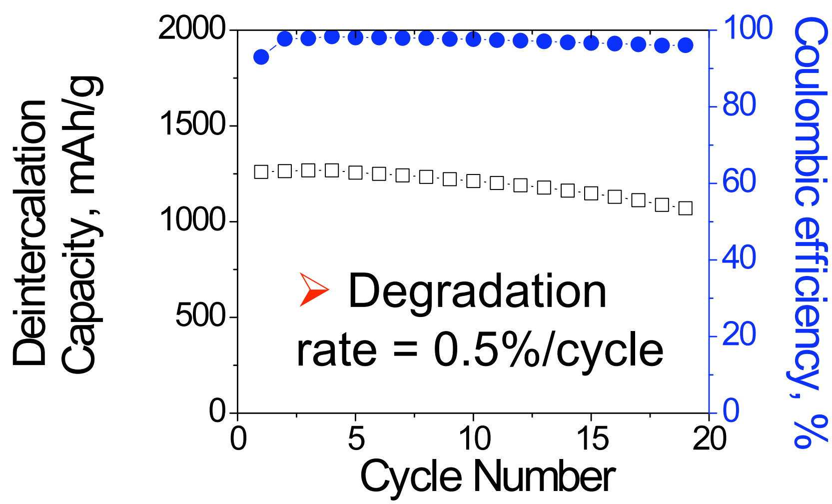
** - provisional US patent filed*

Novel Binders for Si Anodes: Polyvinyl Acids

- UNEXPECTED PROBLEM – new batches of Si nanopowder exhibited lower conductivity and did not work ☹

- SOLUTION: Carbon coatings

- Approaches: (1) CVD, (2) deposition of polymers on the Si surface and pyrolysis



C/10

Capacity is given per weight of active material

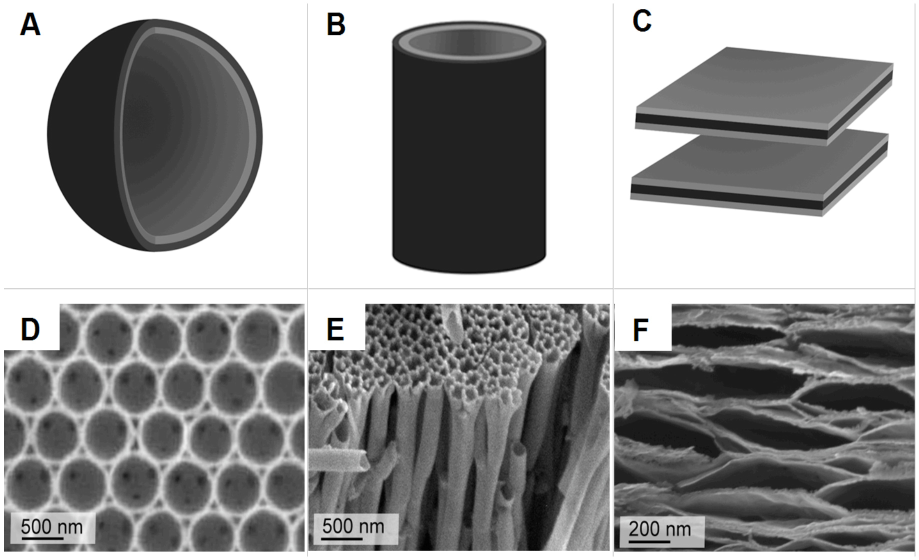
(2) Si-C composite particles which do NOT change volume during Li insertion/extraction

NASA Contract # NNX09CD29P

Porous Si-C Composite Electrodes

- Porous Si-C composite particles may overcome the limitations of non-porous Si-C materials.

- Pre-existing pores will provide the volume needed for Si expansion and allow for fast transport of Li ions

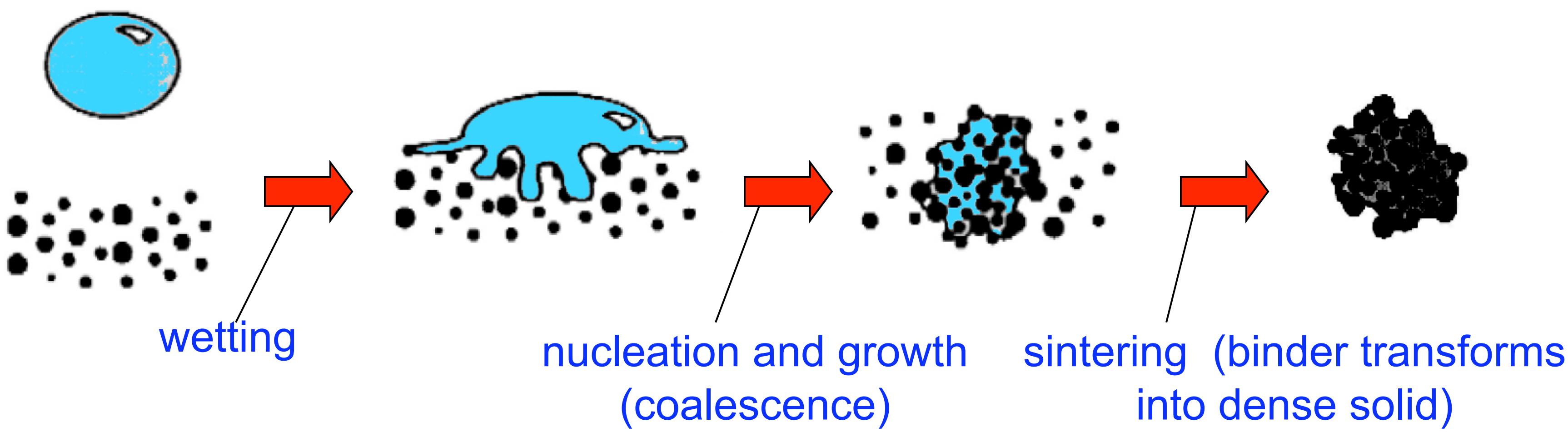


- But... **How to do it?**
- If Si is 10-30 nm for fast Li transport, the porous C should have interconnected pores in the range of ~34-102 nm. **Such carbons** are **not available** commercially
- **Templated C materials – too expensive**
- **Uniform deposition** of Si nanoparticles **inside the narrow pores of large C particles is challenging**

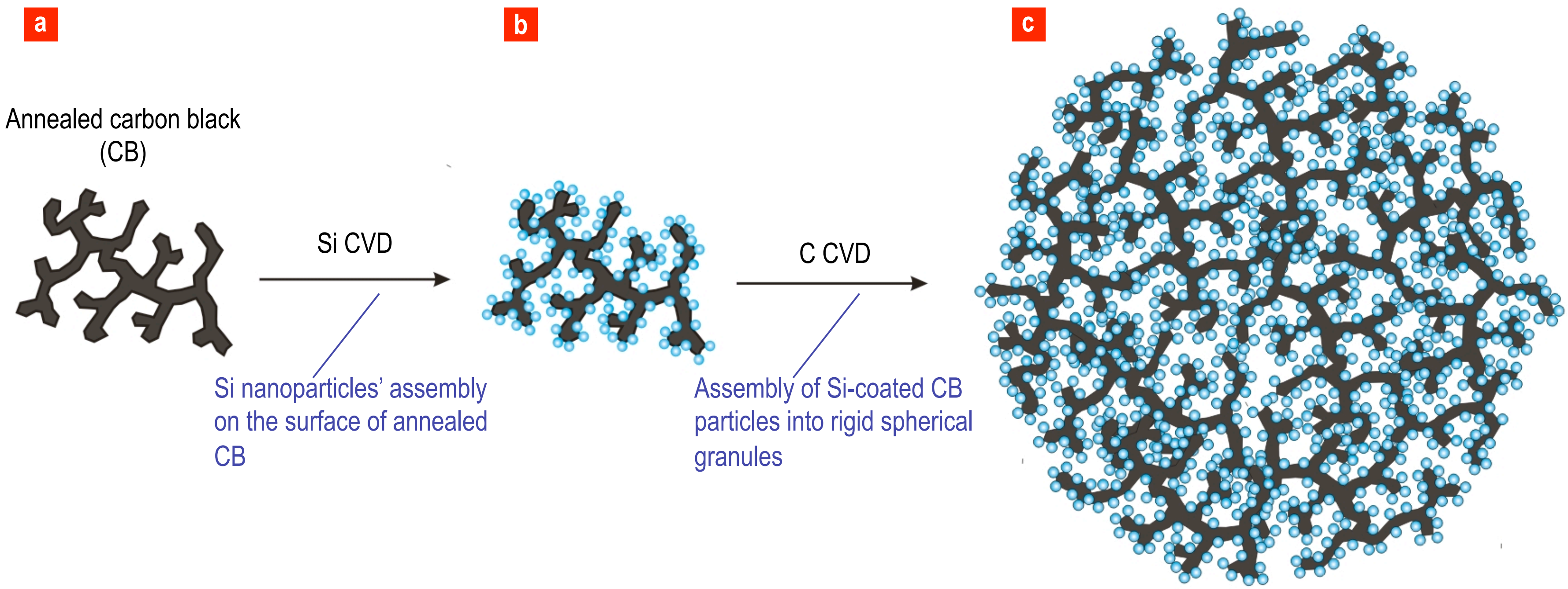
We Need Hierarchical Bottom-up Approach!

- **IDEA**: **deposit** small **Si nanoparticles on** low-cost open **C nanoparticles and self-assemble** them into granules

- Small nanoparticles tend to form adhere to surfaces / agglomerates
- Nanoparticle assemblies can then be formed into spherical granules using a low-cost process, known as **granulation** or **balling**
- **Granulation** is often used in the pharmaceutical and food industries, but it remains uncommon for energy storage applications.



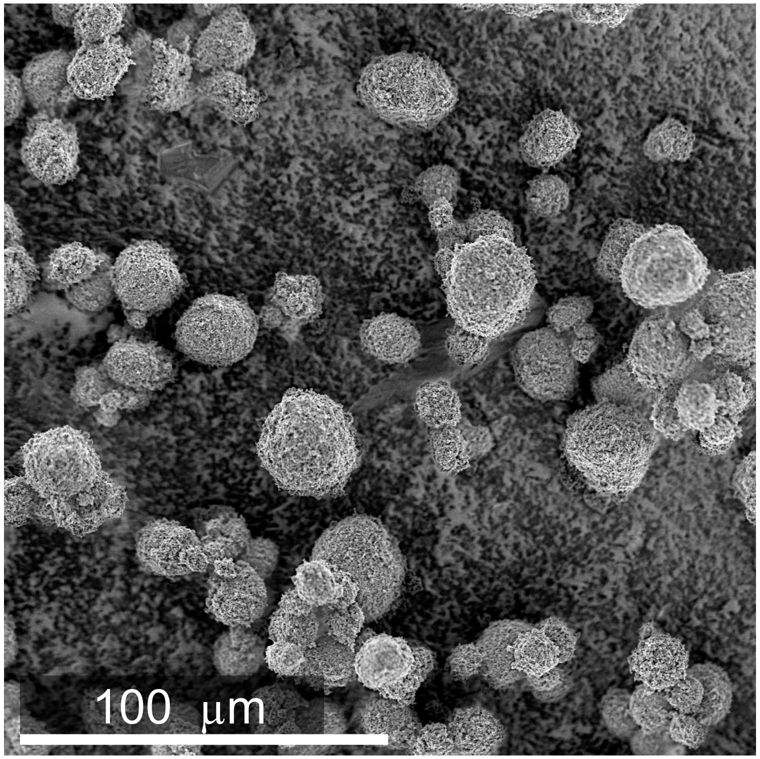
Hierarchical Bottom-up Approach

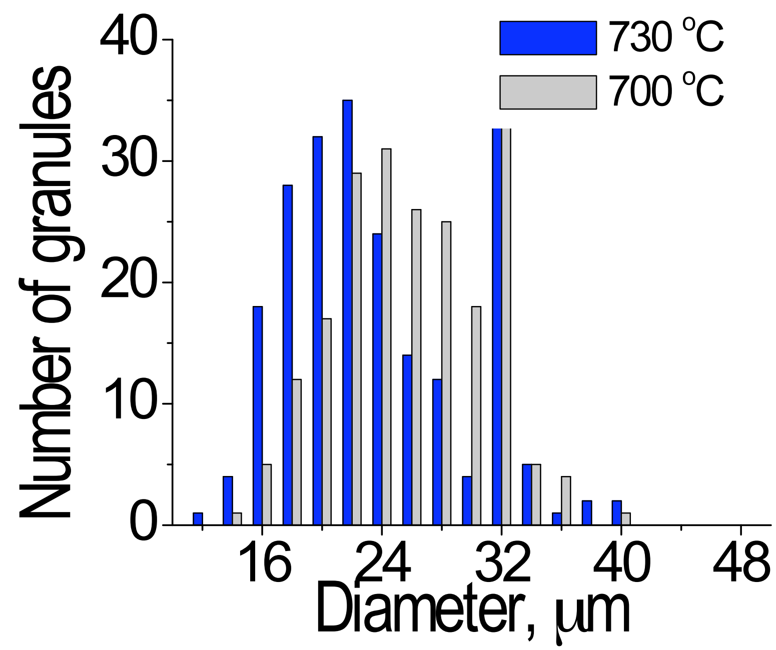


- ➢ Use annealed carbon black (CB): open structure, very low apparent density, high specific surface area (~ 80 m^2/g), ultra-low cost (10 times cheaper than graphite)
- ➢ Si deposition by Chemical Vapor Deposition (CVD): $SiH_4 \rightarrow Si + 2H_2$
- ➢ Use hydrocarbon (propylene) as a binder for granulation: no Si oxidation; transforms into conductive, Li-permeable carbon upon annealing

** - provisional US patent filed*

Hierarchical Bottom-up Approach





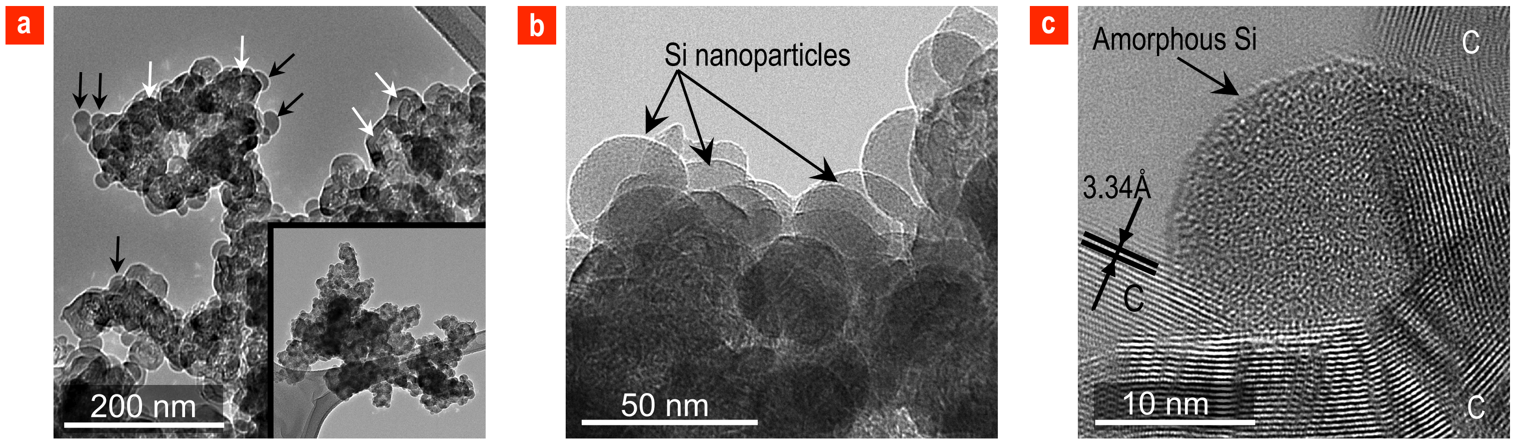
➢ **Control** over the **particle size**, **pore size** and **composition** of the composite:

- Size of Si nanoparticles is determined by Si CVD (time, temperature, pressure)
- Size of Si-C spheres is determined by the granulation process (temperature)
- Pore size is determined by the size of the branches in the nanocarbon, the size of the deposited Si nanoparticles and the amount of the binder

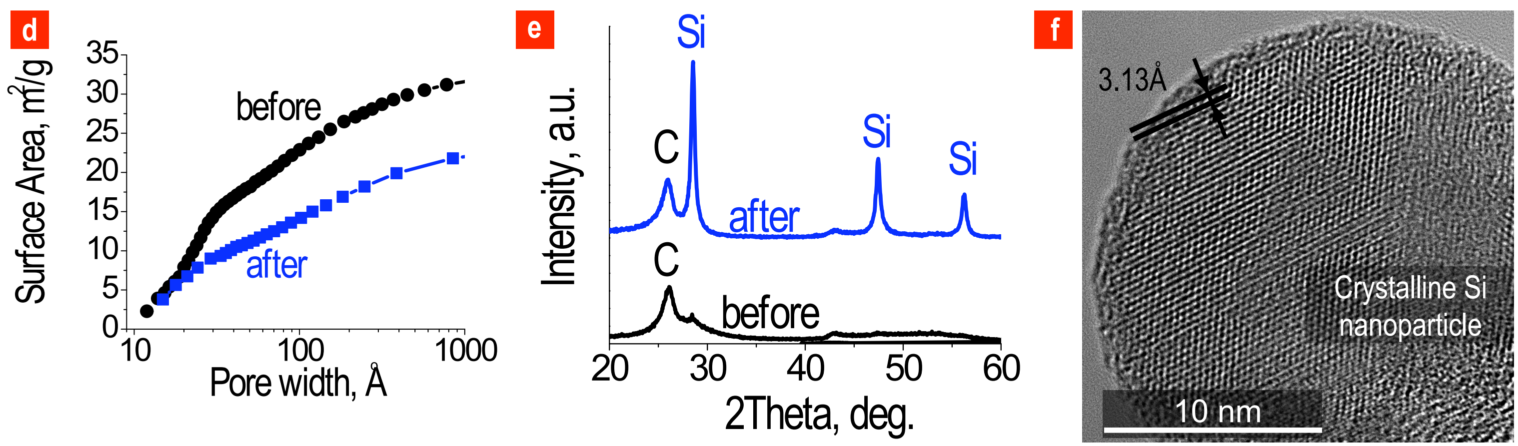
** - provisional US patent filed*

Hierarchical Bottom-up Approach

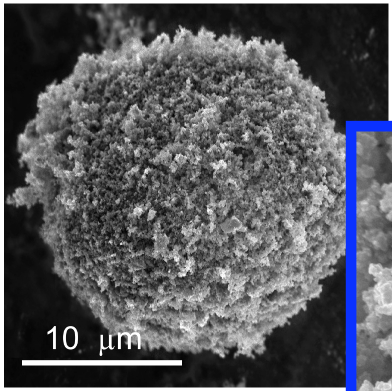
After Si deposition:

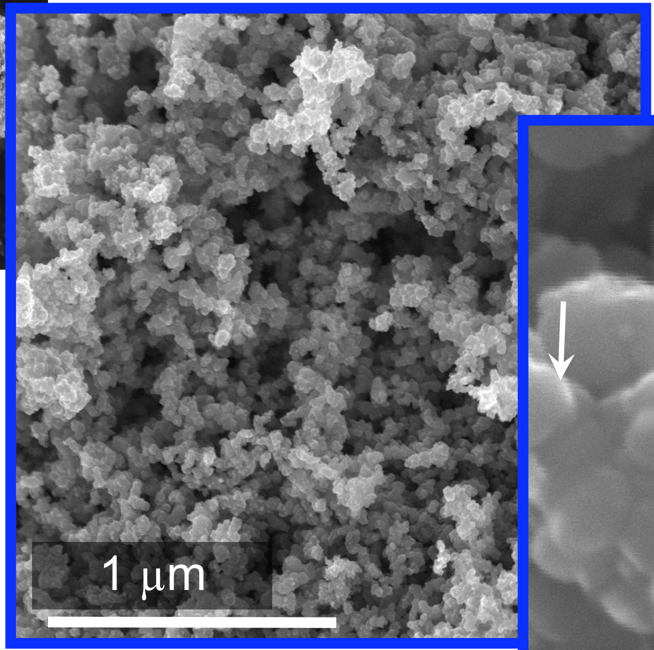


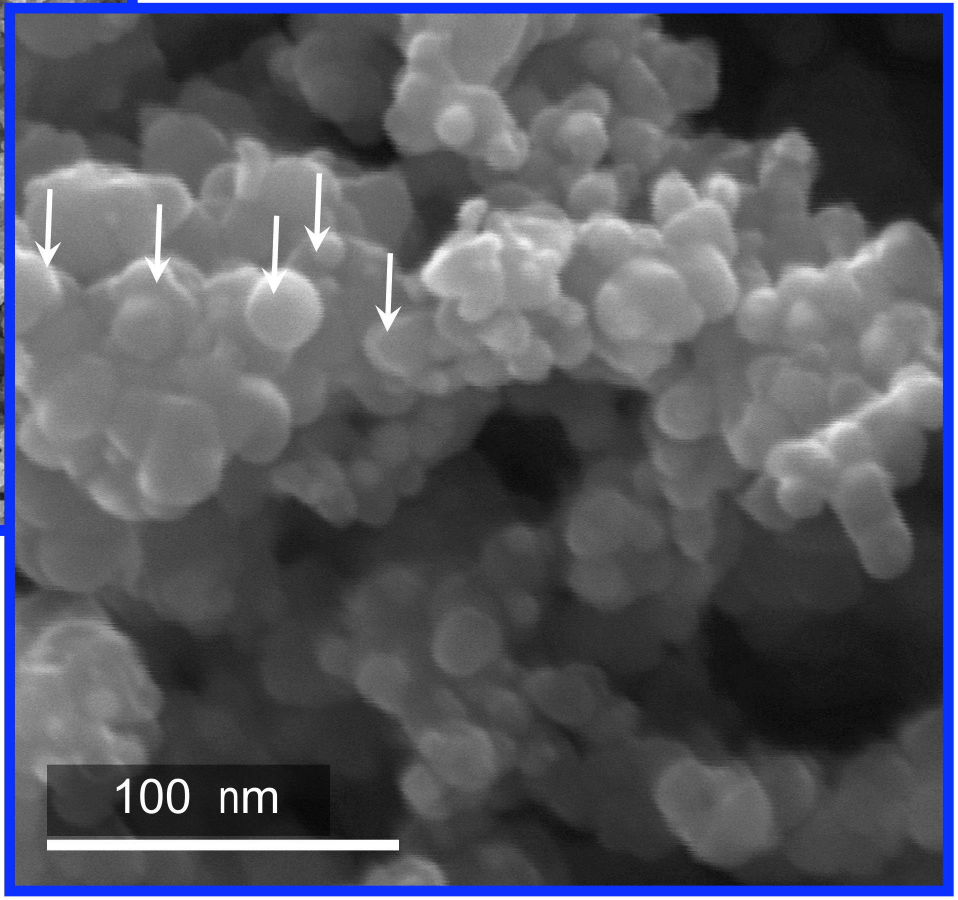
After granulation:



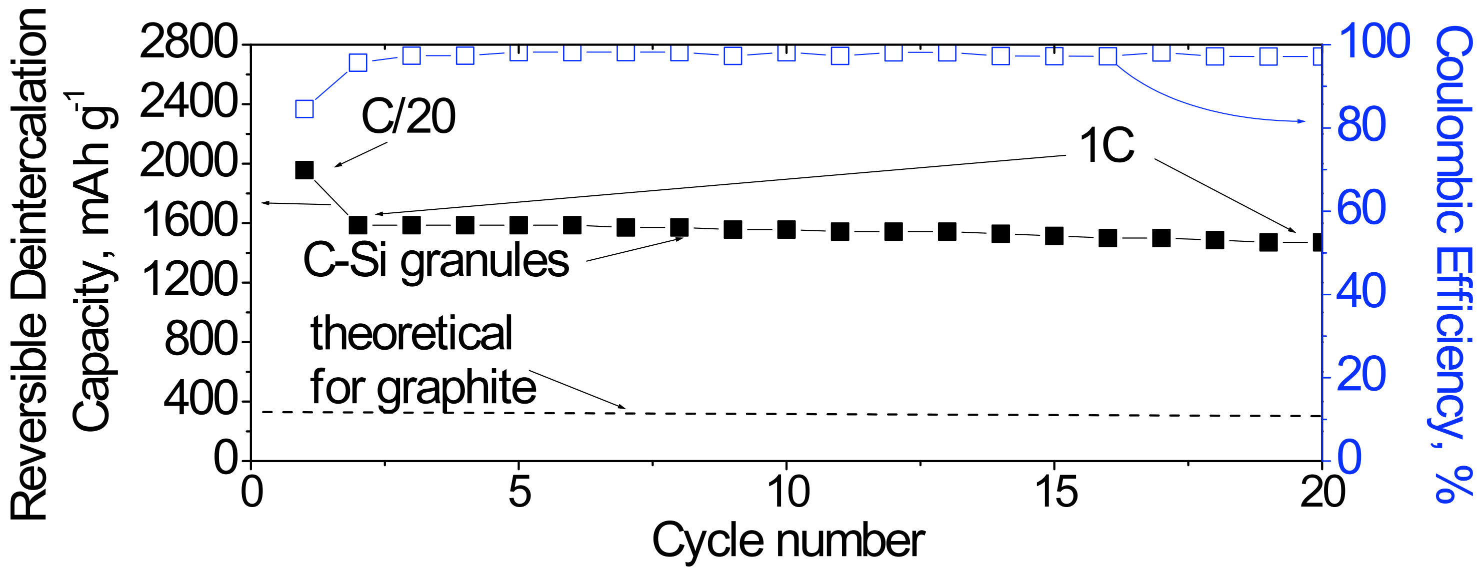
Hierarchical Bottom-up Approach

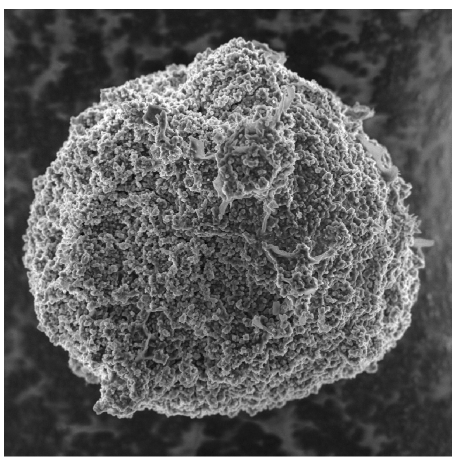


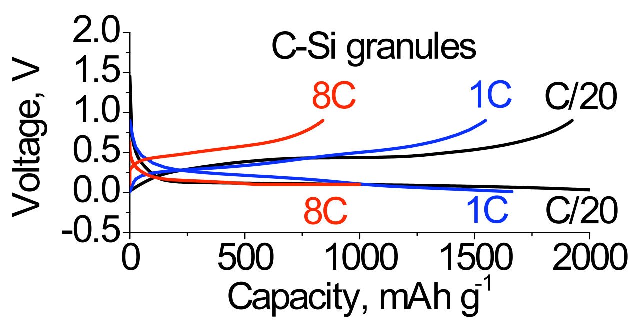


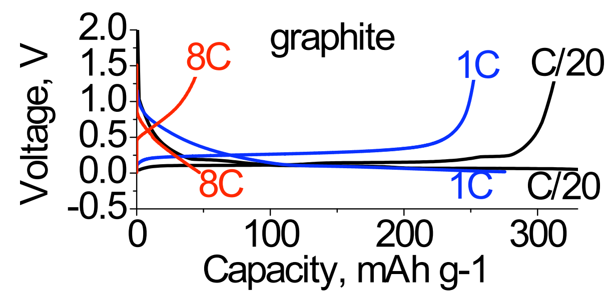


Hierarchical Bottom-up Approach









** - provisional US patent filed*

Hierarchical Bottom-up Approach

- Greatly **improved handling, reduced dustiness, increased bulk density, minimized health hazard**

- The specific reversible deintercalation capacity ~ 1950 mAh/g at C/20: **6 times higher than that for graphitic anodes**

- The specific capacity of the Si nanoparticles alone was estimated as ~ 3670 mAh/g, which is the **highest value ever reported for nanoparticles**.

- The pores available in the composite granules for Si expansion during Li insertion allowed for efficient and **stable anode performance**

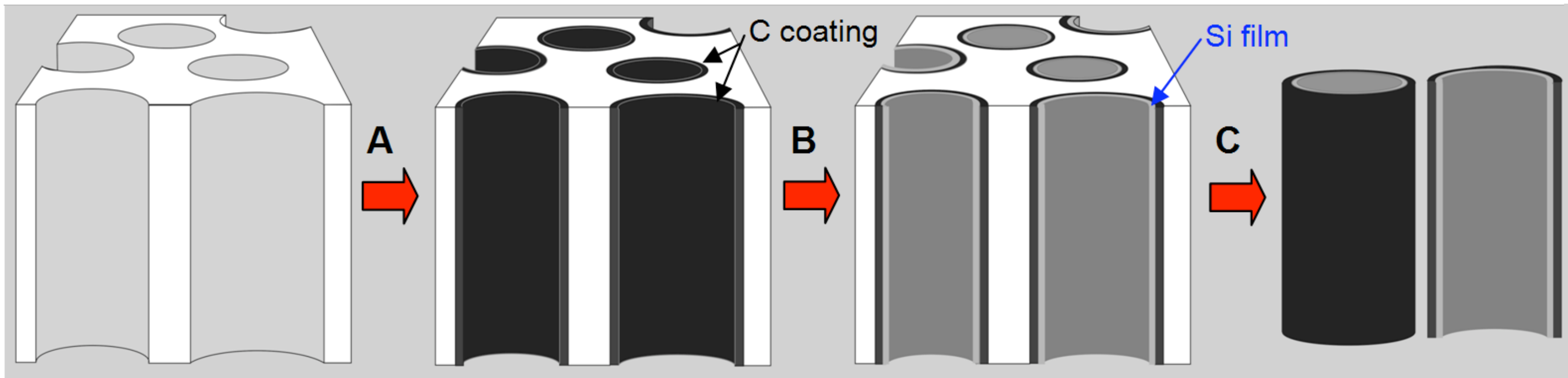
- Outstanding high rate capability. For the same specific current value (2.98 A/g), our C-Si electrodes showed capacity in excess of 1500 mAh/g, which is over 37 times higher than that for graphites of comparable size.

(3) Binder-FREE electrodes

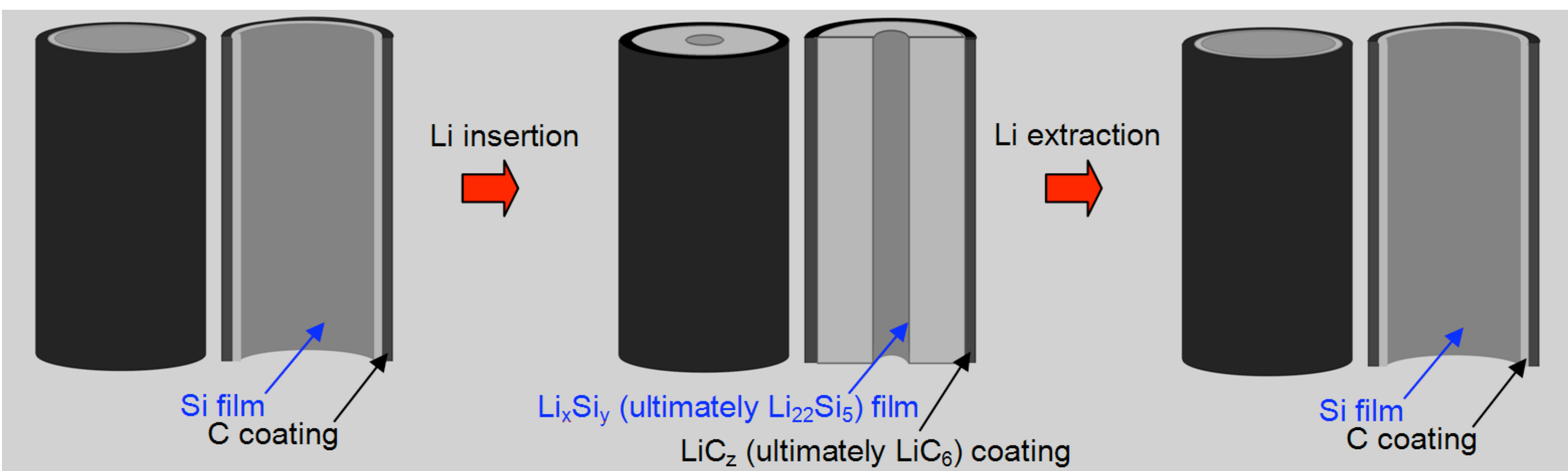
No NASA Contract ☹

Effect of curvature and Si-C interphase

Synthesis:



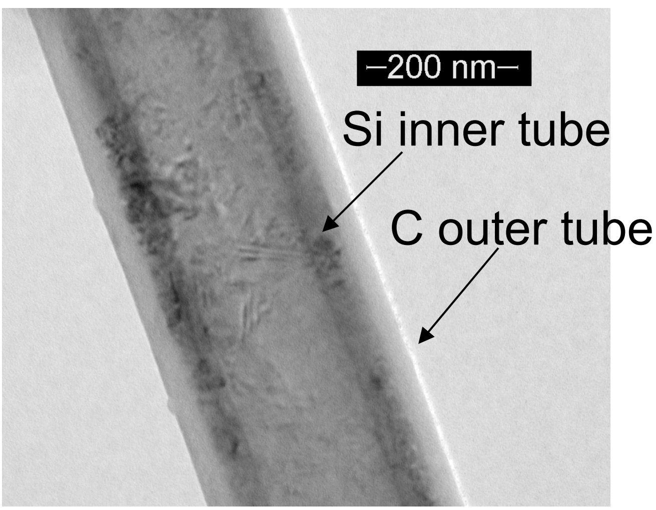
Idealized performance:

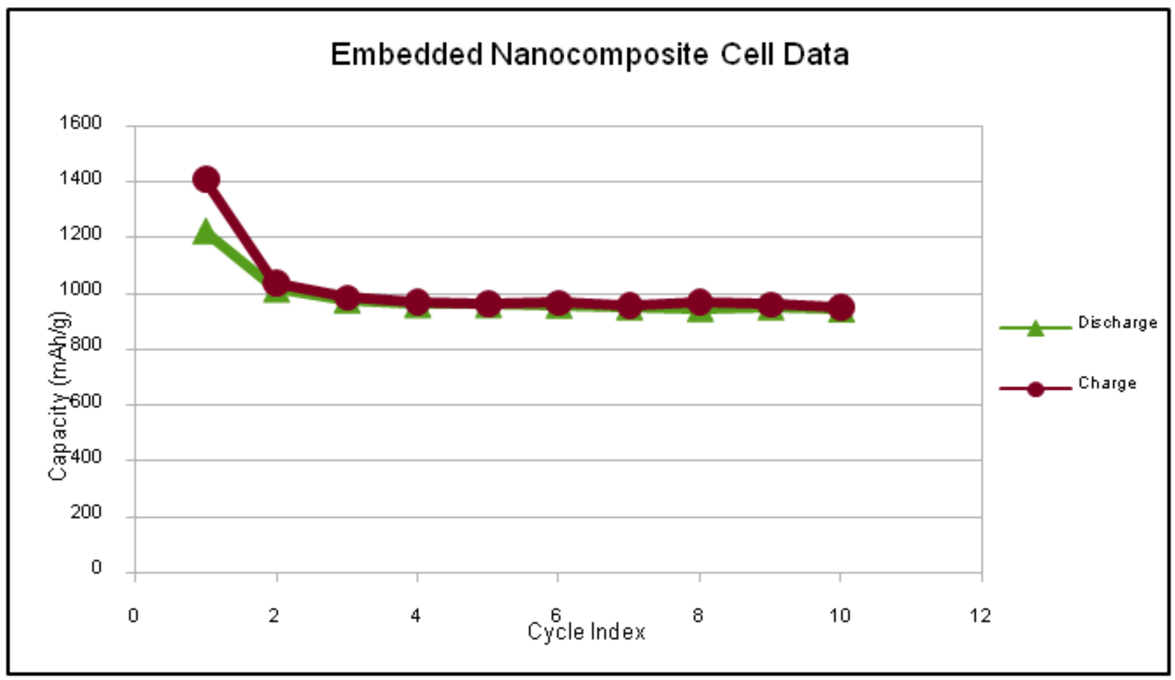


Effect of curvature and Si-C interphase

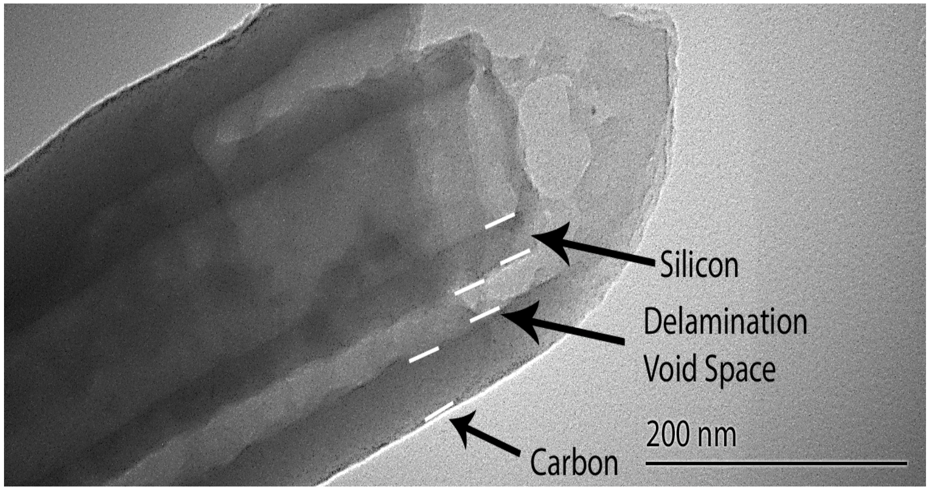
- Si expands upon Li insertion and C does not. Will continuous interphase survive? Under what conditions?

- What is the effect of curvature? Positive vs. negative?



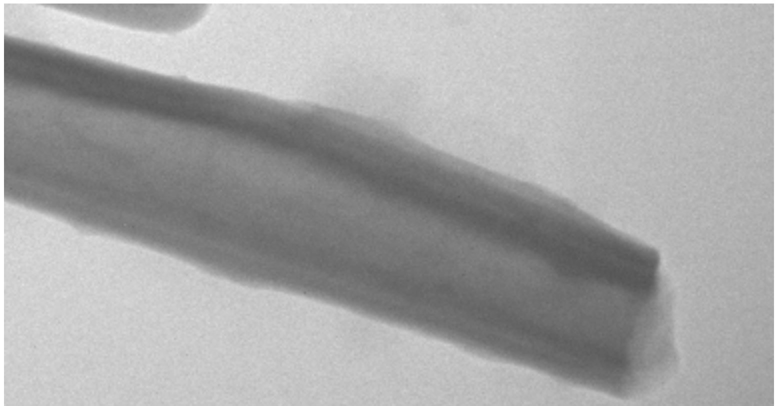


Effect of curvature and Si-C interphase



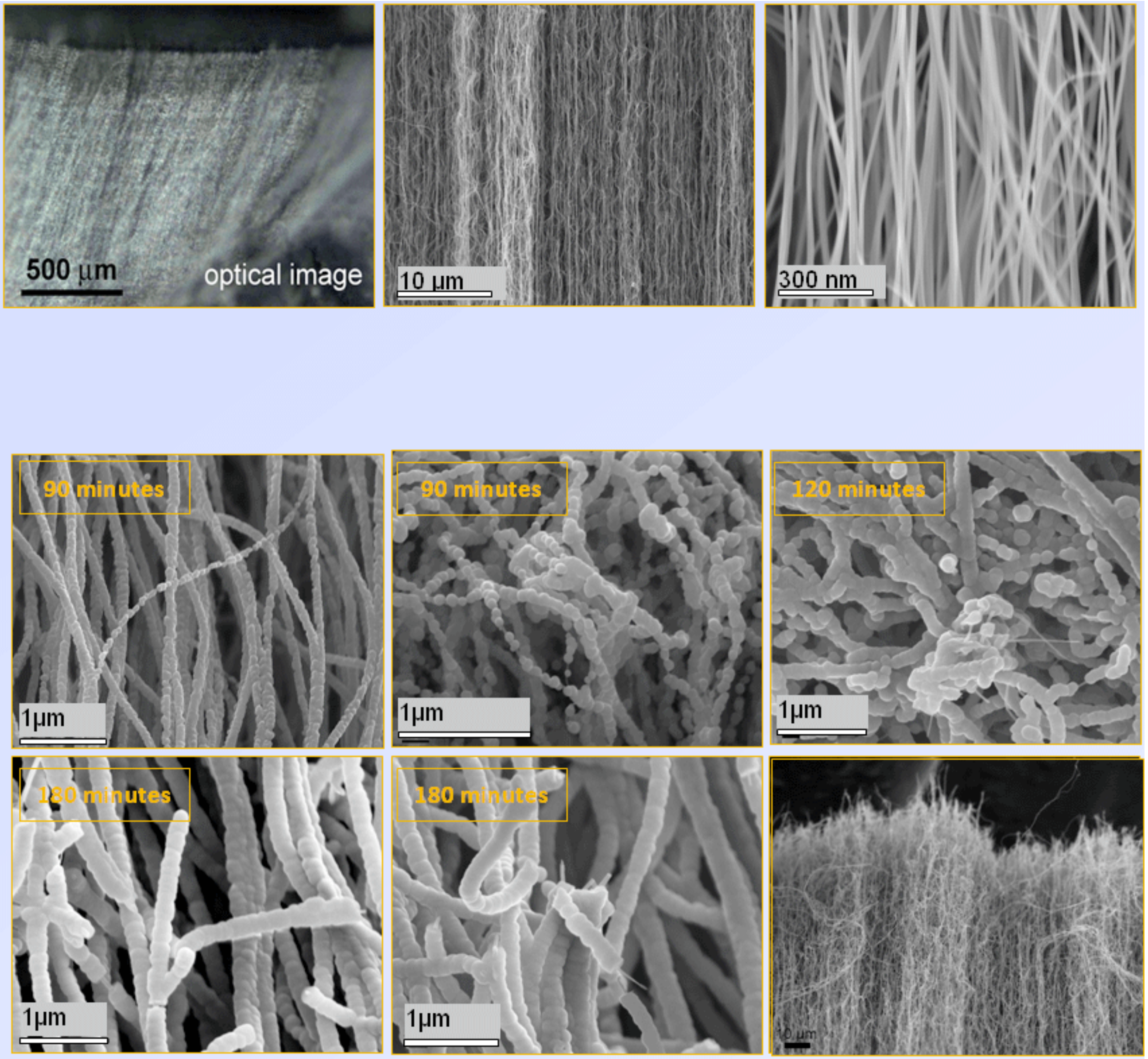
- Inner Si tube compresses and delaminates from the outer C tube after cycling

- However, it does NOT happen for either thin Si coating or for Si coating the external surface of CNT



No compression and delaminating

VANTA coated by Si



Multi-walled VACNTA:

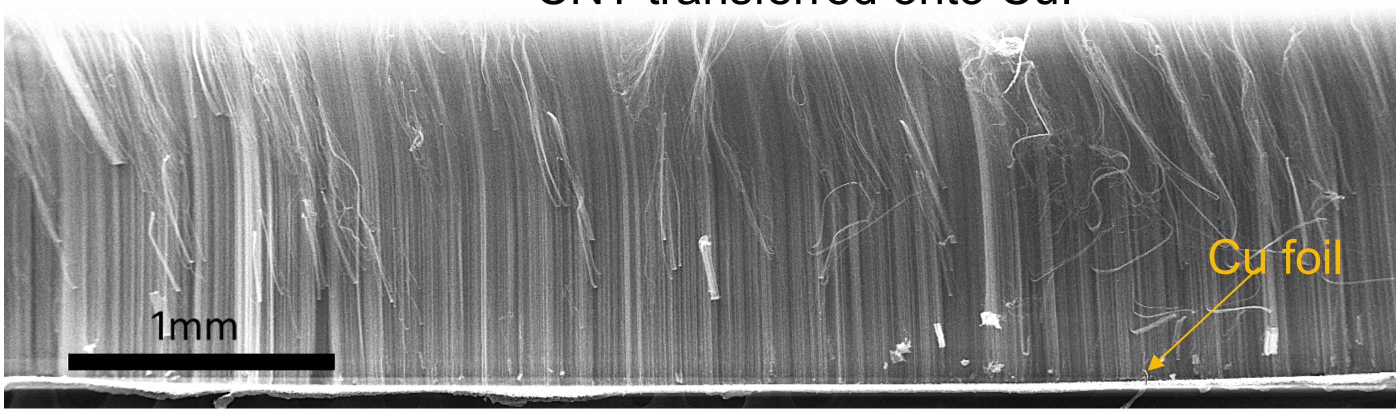
- Acetylene precursor
- Water vapor was used to stabilize the growth
- Growth rate > 0.1 mm/min allows for low cost VACNTA synthesis

- CVD coating by Si

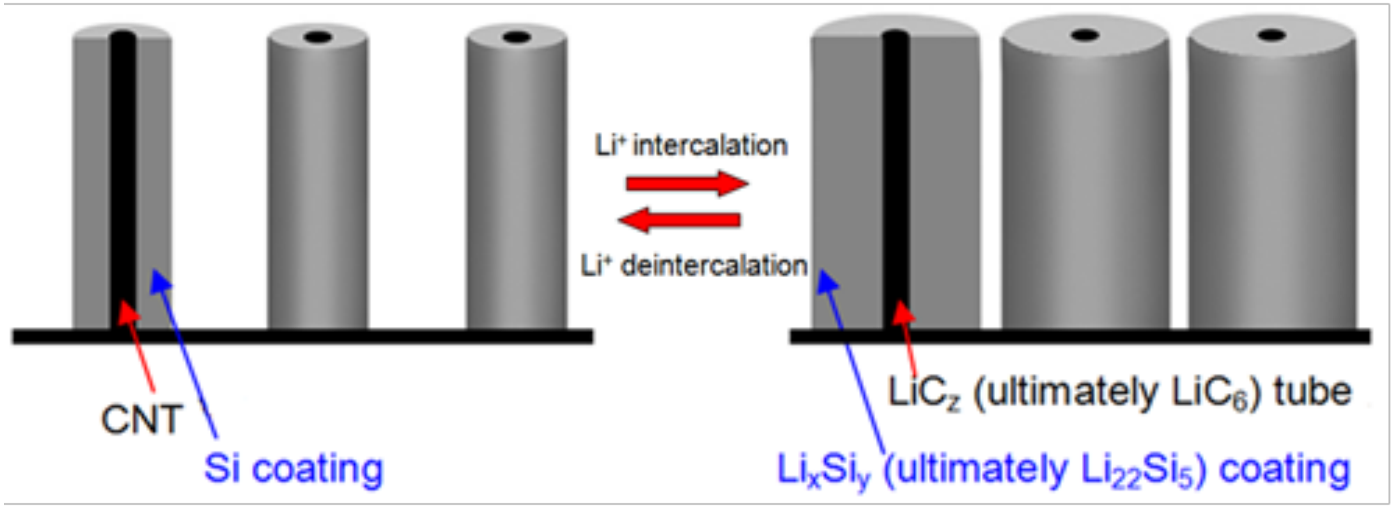
(collaboration with Jud Ready, GTRI)

VANTA coated by Si

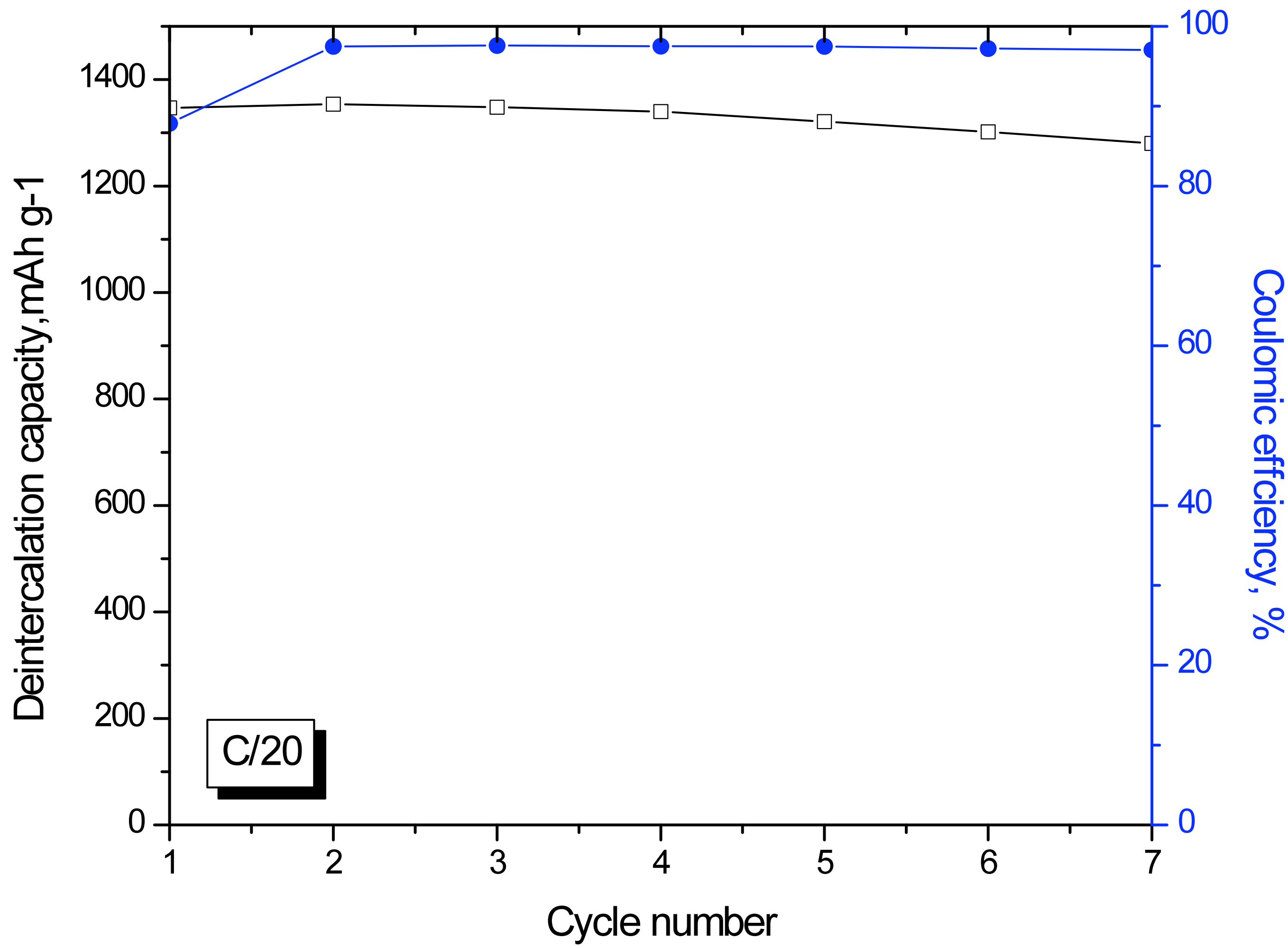
CNT transferred onto Cu:



Idealized performance:



VANTA coated by Si

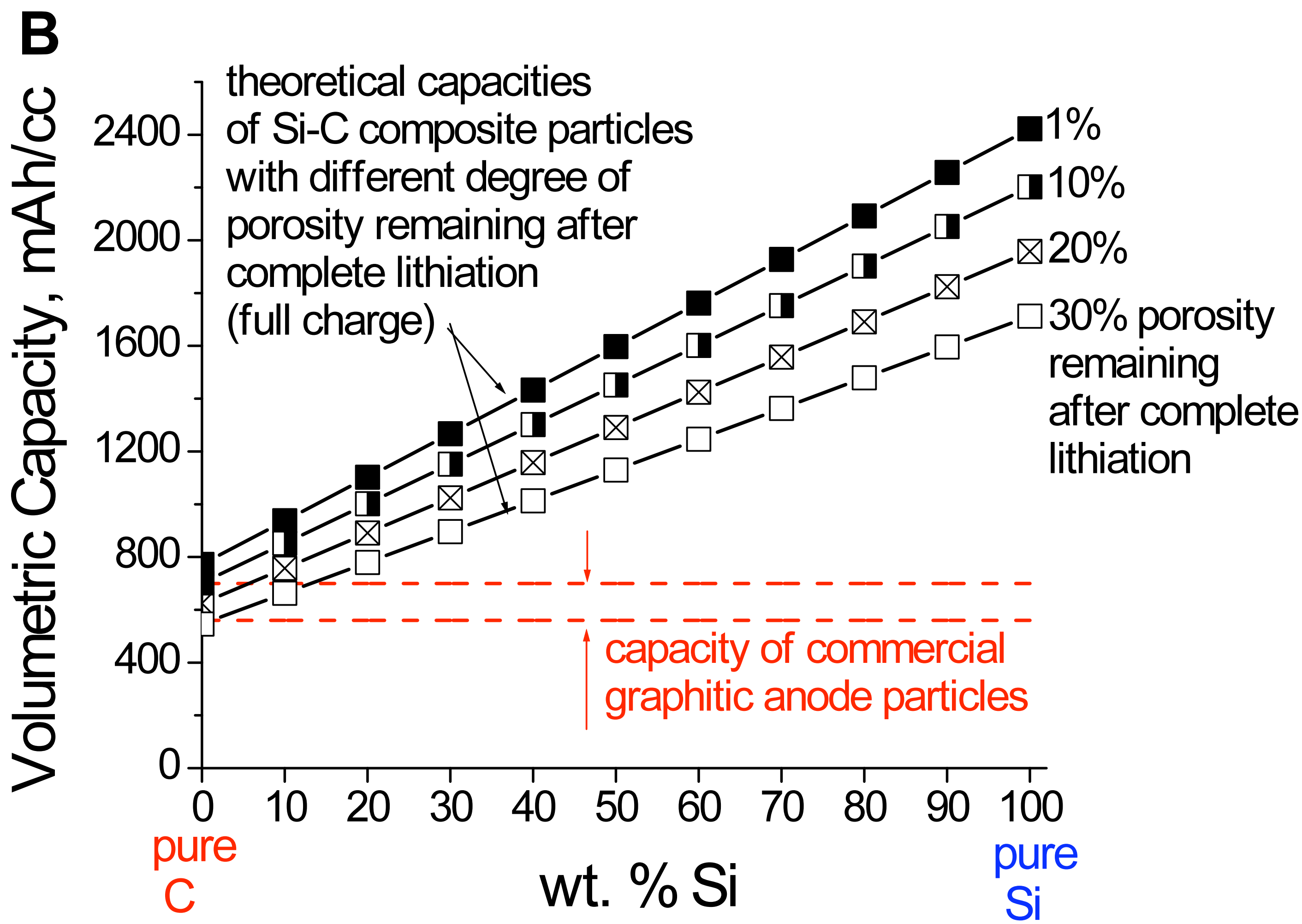


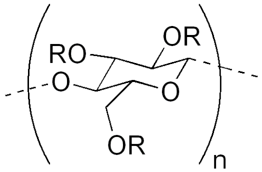
Thank you for your attention!

Acknowledgement

- NASA
- Organizers (Dr. Concha Reid)

Additional Slides


B
Volumetric Capacity, mAh/cc
0
400
800
1200
1600
2000
2400
theoretical capacities
of Si-C composite particles
with different degree of
porosity remaining after
complete lithiation
(full charge)
1%
10%
20%
30% porosity
remaining
after complete
lithiation
capacity of commercial
graphitic anode particles
0
10
20
30
40
50
60
70
80
90
100
pure
C
wt. % Si
pure
Si



R = CH_2-COOH

- Need to use water
- Can NOT change mechanical properties
- Fewer # of functional groups

CMC